

(12) UK Patent Application (19) GB (11) 2 261 218 (13) A

(43) Date of A publication 12.05.1993

(21) Application No 9123402.1

(22) Date of filing 05.11.1991

(71) Applicant
Rhône-Poulenc Chemicals Limited

(Incorporated in the United Kingdom)

Oak House, Reeds Crescent, Watford,
Hertfordshire, WD1 1QH, United Kingdom

(72) Inventors
John Frederick Carr
Patrick Royston Bryan
Mark Timothy Hopwood

(74) Agent and/or Address for Service
J A Kemp & Co
14 South Square, Gray's Inn,
London, WC1R 5LX, United Kingdom

(51) INT CL⁵
C07C 229/16, C11D 3/33

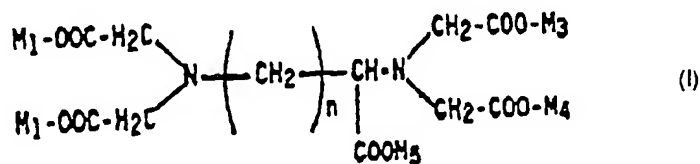
(52) UK CL (Edition L)
C2C CAB CLU C20Y C29Y C292 C30Y C32Y C323
C366 C367 C45Y C456 C630 C648 C80Y C807
C5D DEX D107 D108 D110 D111 D116 D120 D121
D144 D153 D166 D180
U1S S1353 S1427

(56) Documents cited
Chemical Abstracts 112(12): 106135u
Chemical Abstracts 109(26):238263g
Chemical Abstracts 109(18):157410a
Chemical Abstracts 106(4):23955m
Chemical Abstracts 102(6):51722u
Chemical Abstracts 97(2):8578t
Chemical Abstracts 87(4):29839n
Chemical Abstracts 105 (23): 208376w
Chemical Abstracts 102 (5): 46238m
Chemical Abstracts 100 (13): 103831j
Chemical Abstracts 93 (8): 81513q
Chemical Abstracts 86 (18): 128301s

(58) Field of search
UK CL (Edition K) C2C CLU, C5D DEX
INT CL⁵ C07C, C11D
Online database: CAS ONLINE

(54) Biodegradable sequestrants for detergent compositions

(57) Detergent compositions for domestic use or for industrial use, are characterised in that they comprise at least one biodegradable sequestrant of formula (I)



in which:

- n is from 1 to 6,
- the symbols M₁, M₂, M₃, M₄ and M₅, identical or different, represent a hydrogen atom, an alkali metal, an ammonium group -NH₄ or an ammonium group substituted by 1 to 4 hydrocarbon groups. The compounds of formula I may be prepared from the corresponding diamine.

BIODEGRADABLE SEQUESTRANTS FOR DETERGENT COMPOSITIONS

The present invention relates to the use of biodegradable sequestrants in detergent compositions, as well as to a process for preparing such
5 sequestrants.

Numerous domestic or industrial detergent compositions contain oxygen-containing bleaching agents such as in particular sodium perborate or sodium percarbonate.

10 It is known that the efficiency of these bleaching agents in detergent compositions is reduced when the water used for the washing or the materials that are to be washed contain metal ions such as for example manganese, copper and iron ions. These ions
15 react with the bleaching agents containing peroxides or generating peroxides, thus causing the partial decomposition of the said bleaching agents and, consequently, the reduction in their concentration during the washing operation.

20 Other components of the detergent compositions may also be decomposed or deactivated by metal ions.

The incorporation of sequestrants makes it possible to avoid or to limit the decomposition of the
25 bleaching agents and the decomposition or the deactivation of other components such as enzymes or brighteners.

A tendency also exists to incorporate in the detergent compositions compounds of natural origin such as surface-active agents derived from vegetable oil. These compounds can undergo decomposition catalysed by
5 traces of metals. The presence of sequestrants of metal ions therefore also enables their preservation.

Finally, the detergent compositions contain builders which have the essential role of complexing the calcium and magnesium ions present in hard waters
10 and therefore of maintaining them in solution. The presence of builders generally prevent the deposition or the precipitation of insoluble calcium and/or magnesium compounds, and more particularly their deposition on the clean surface of the item to be
15 cleaned.

In this manner, a greater proportion of the surface-active agents of the detergent compositions remains available and the efficiency of the compositions is thereby improved.

20 Among the actual sequestrants and the builders normally used, ethylenediaminetetraacetate acid and its sodium derivatives (EDTA), nitrilotriacetic acid (NTA), phosphates and phosphonates may be mentioned.

25 EDTA and other similar compounds exhibit a good complexing power for heavy metals, but suffer from the major disadvantage of their very low biodegradability, which may lead to their banning, at

least partially, in future.

NTA is suspected of being carcinogenic and/or teratogenic and its use is banned for detergent compositions in some states in the United States and in
5 some European countries.

Phosphates, such as in particular sodium tripolyphosphate, end up, in the absence of a plant for sewage purification, in water courses and in lakes where they accelerate the growth of algae; they are
10 therefore currently accused of participating in the phenomenon of eutrophication of lakes and water courses.

The use of aminoethylene phosphonates appears to pose a similar problem.

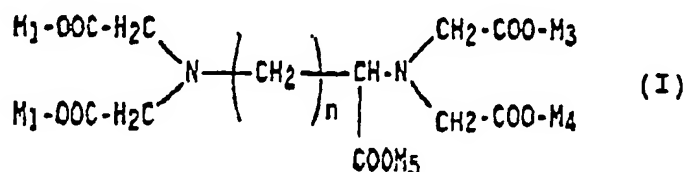
15 In order to remedy these disadvantages, other complexing agents exhibiting better biodegradability have been proposed.

Thus, Patent EP-A-0 287, 885 describes the use of N,N-bis(carboxymethyl)-2-amino-2-
20 hydroxymethylacetic acid and its alkali metal, ammonium and substituted ammonium salts, as complexing agents in detergent compositions containing a bleaching agent.

Patent US 4,827,014 relates to the use of compounds which are isomers of the preceding compounds,
25 N,N-bis(carboxymethyl)-3-amino-2-hydroxypropionic acid and its alkali metal, ammonium and substituted ammonium salts in the same type of detergent compositions.

New research initiated by the applicant has led to the present invention.

The latter thus relates to detergent compositions for domestic use or for industrial use, characterised in that they comprise at least one sequestrant
10 chosen from the compounds of general formula (I)



in which:

- 15 - n represents a number from 1 to 6,
 - the symbols M_1 , M_2 , M_3 , M_4 and M_5 , identical
 or different, represent:
 • a hydrogen atom,
 • an alkali metal,
 • an ammonium group $-NH_4$ or an ammonium
20 group substituted by 1 to 4 organic
 groups.

Preferably, in the formula (I) of the sequestrants used:

- n represents a number from 1 to 6,
- the symbols M_1 , M_2 , M_3 , M_4 and M_5 , identical or different, represent:
 - a hydrogen atom,
 - a sodium or potassium atom,
 - an NH_4 group,
 - a monoalkylammonium, dialkylammonium, trialkylammonium or tetraalkylammonium group, the alkyl radical or radicals, linear or branched, having 1 to 4 carbon atoms.

In the detergent compositions of the invention, a sequestrant or sequestrants of general formula (I) will be preferably used, in which:

- n represents a number from 2 to 4,
- the symbols M_1 , M_2 , M_3 , M_4 and M_5 , identical or different, represent a hydrogen atom or a sodium atom.

As nonrestrictive examples of sequestrants of formula (I), there may be mentioned the pentasodium or tetrasodium salts of N,N,N',N' -tetra(carboxymethyl)-2,6-diaminohexanoic acid, the pentasodium or tetrasodium salts of N,N,N',N' -tetra(carboxymethyl)-2,5-diaminopentanoic acid, the pentasodium or tetrasodium salts of N,N,N',N' -tetra(carboxymethyl)-2,4-diaminobutyric acid.

The sequestrants of formula (I) may be either levorotatory (L), dextrorotatory (D) or DL.

Mixtures of several sequestering agents of formula (I) may also be used without departing from the framework of the invention.

5 The amount of sequestrant of formula (I) in the detergent compositions may vary widely, in particular depending on the type of detergent composition.

Generally, the sequestrant of formula (I) represents 0.01 % to 20 % and preferably 0.05 % to 10 %
10 by weight relative to the total dry weight of the detergent composition.

Total dry weight of the detergent composition, in the present account, is understood as meaning the total weight of the various constituents of
15 the said detergent composition with the exception of the water optionally present in particular in liquid detergent compositions.

As previously indicated, the amount of sequestrant of formula (I) in the detergent
20 compositions varies depending on whether their role is that of avoiding or slowing down the decomposition of the bleaching agents of the perborate type, or of replacing all or part of the builders present in the said detergent compositions.

25 When the sequestrant of formula (I) is present essentially in order to avoid the decomposition of the bleaching agents, amounts of 0.05 % to 2 % by weight per total dry weight of the detergent

composition are sufficient.

In contrast, if it is desired to replace at least part of the builders in the detergent composition by the sequestrant of formula (I), the amount of the
5 latter will be most often 1 % to 20 %.

In the industrial detergent compositions used in particular for washing hard surfaces like metal surfaces, glass, car bodies, the role of the sequestrant of formula (I) is more particularly to form
10 a complex with calcium ions and it may, in that case, represent 0.01 % to 5 % by weight per weight.

The detergent compositions also normally contain various constituents which may differ depending on the type of detergent composition.

15 Thus, as a guide, they normally contain about 5 to 25 % by weight per weight of surface-active agents, 15 to 50 % by weight per weight of builders (part of which at least may consist of the sequestrants of formula (I)), with or without co-builders, 5 to 35 %
20 by weight per weight of bleaching agents with or without activators of the said bleaching agents, and other constituents such as enzymes, antifoaming agents, corrosion inhibitors, brighteners, perfumes, colorants, formulation adjuvants, fillers and, optionally, water.

25 The surface-active agents which are generally suitable in the detergent compositions contain one or more anionic, zwitterionic or nonionic hydrophilic organic radicals.

Among the anionic surface-active agents, sulphonates, sulphates and carboxylates may be mentioned in particular. The sulphonates are more particularly alkylbenzenesulphonates, alkylsulphonates, 5 hydroxyalkylsulphonates and esters of sulphonated fatty acids. The sulphates are more particularly sulphuric monoesters of primary alcohols or secondary alcohols, sulphates of fatty alkanolamines, of fatty acids monoglycerides or of the reaction products of ethylene 10 oxide with primary or secondary fatty alcohols or alkylphenols. The carboxylates are more particularly fatty esters or amides of hydroxycarboxylic or aminocarboxylic acids. These anionic surface-active agents may be present in the form of their sodium, 15 potassium or ammonium salts or of organic bases like monoethanolamine, diethanolamine and triethanolamine.

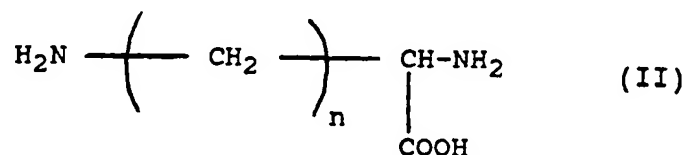
The nonionic surface-active agents may be for example condensation compounds of 3 to 40 moles of ethylene oxide per mole of fatty alcohol, alkylphenol, 20 fatty acid, fatty amine, fatty acid amide or alkanesulphonamide.

The builders normally used in the detergent compositions are more particularly sodium carbonate, sodium silicate, phosphates like sodium pyrophosphate, 25 sodium tripolyphosphate, the other sodium polyphosphates or sodium metaphosphate, alkane-polyphosphonates, aminoalkanepolyphosphonates, hydroxyalkanepolyphosphonates, phosphonocarboxylates or

zeolites. The builders are frequently combined with co-builders like carboxylic polyacids such as polymers of acrylic acid, maleic acid, itaconic acid, mesaconic acid, aconitic acid, methylenemalononic acid or
 5 citraconic acid; carboxymethyl ethers of sugars, starch and cellulose may also be mentioned as co-builders.

The bleaching agents are in particular peroxide derivatives like for example hydrated sodium perborates, peroxycarbonates, peroxyphosphonates.
 10 Activators of these bleaching agents are often used; they are for example N-acylated or O-acylated compounds.

The sequestrants of formula (I) may be obtained in particular from diaminocarboxylic acids of
 15 general formula (II):



in which n represents a number from 1 to 6 and preferably from 2 to 4, by reaction with sodium chloroacetate.

20 Generally, the reaction is carried out in solution in water and at a temperature of 25°C to 100°C and preferably 40°C to 90°C without these values having a critical importance.

Among the diaminocarboxylic acids of
 25 formula (II), lysine (n = 4) is very particularly

advantageous because of its relatively low cost.

Ornithine ($n = 3$) and 2,4-diaminobutyric acid ($n = 2$) may also be mentioned.

Lysine and ornithine are the two preferred
5 diaminocarboxylic acids of formula (II) enabling the preparation of the most advantageous sequestrants of formula (I) both for their sequestering qualities and for their biodegradable character.

Another process for preparing the
10 sequestrants of formula (I) consists in reacting diaminocarboxylic acid with an alkali metal cyanide and formaldehyde.

This reaction is normally carried out in water, in a water-miscible solvent or in a mixture of
15 water and such a solvent, at a temperature of 25°C to 100°C and preferably 40°C to 90°C. If water is present during the reaction then the sequestrant of formula I may be formed directly by this reaction. If water is not present and the solvent is e.g. a water-miscible solvent,
20 then a nitrile compound is produced, which is then hydrolysed to give the desired compound. The hydrolysis may be carried out in situ or after isolation of the nitrile compound.

The following examples illustrate the invention.

Example 1

Preparation of the pentasodium salt of N,N,N',N'-tetra(carboxymethyl)-2,6-diaminohexanoic acid

5 146 g (1 mol) of lysine were dissolved in
400 g of water and the solution obtained was heated to
65°C.

480 g (4.12 mol) of sodium chloroacetate were
added in portions in 1 hour with stirring.

10 600 g of an aqueous solution containing 27 %
by weight of sodium hydroxide (4.05 mol of NaOH) were
then progressively added at a rate enabling the pH to
be maintained between 8.8 and 9.2. During the addition
of sodium hydroxide, the temperature was allowed to
15 rise up to a maximum of 85°C.

At the end of the addition, the reaction
mixture was again stirred for 2 hours at 88°C and then
the temperature was raised to the reflux temperature
for 30 minutes.

20 The reaction mixture was allowed to cool to
room temperature; sodium chloride precipitated during
this cooling. Next, the mixture was filtered at room
temperature.

The filtrate was allowed to stand overnight
25 and another amount of sodium chloride then
precipitated.

After another filtration, the filtrate was diluted with 1500 g of water, it was then acidified to about pH 1 with 800 g of hydrochloric acid at 36 % by weight.

5 After inoculation by seeding, the crystallisation occurred slowly. After allowing to stand overnight, the product was filtered, washed abundantly with water and finally suspended in 1000 g of water and heated with stirring at 80°C.

10 After cooling, the solid was filtered and dried at 80°C under vacuum.

250 g of N,N,N',N'-tetra(carboxymethyl)-2,6-diaminohexanoic acid with a melting point of 216-220°C were thus obtained
15 (yield of 66 % relative to the lysine used).

The corresponding pentasodium salt is easily prepared by neutralising the different carboxylic functional groups by means of a solution of sodium hydroxide.

Example 2

305.5g of lysine was dissolved in 600 mls of water and, 161.2g of 100 TW (47%) sodium hydroxide solution, and 10.8g of sodium cyanide solution (30%) were then added.

The contents of the flask were heated to 67°C - 70°C, and sodium cyanide solution (1572g) and formaldehyde solution (929.2g) were then added continuously over a period of 5.5 hours via peristaltic pumps.

During the early stages of the addition an exotherm produced by the reaction of the cyanide and formaldehyde was sufficient to bring the temperature of the reaction mixture to 97°C - 98°C. The bulk of the addition was carried out at the boiling point at atmospheric pressure.

After all the cyanide had been added, the formaldehyde addition was stopped and the cyanide level of the reaction mixture was checked and found to be 3050 ppm. This level was reduced to below 3 ppm by addition of formaldehyde (to a total of 929.2g)

Throughout the addition, ammonia solution was distilled from the reaction and a total of 1610 ml was collected.

The weight of solution remaining at the end of all additions was 1700g with an initial N,N,N',N'-tetra(carboxymethyl)-2,6-diaminohexanoic acid [Lysta] content of 44%. This was diluted to give a solution of nominally 30% Lysta (Acid).

Final Weight	2636 g
Final Assay	29.6 % Lysta (Acid)

Example 3Complexing power of the sequestrants of
formula (I)

5 The capacity of a sequestrant to fix metal
ions such as Fe, Cu or Ca and to inhibit their effect
may be measured for example by the following method.

 A suitable amount of the sequestrant to be
tested (T.S.) is dissolved in 100 cm³ of water. The pH
is adjusted to 10 by means of a N solution of sodium
10 hydroxide and maintained at this value during the
titration by successive additions of N solution of
sodium hydroxide.

 This solution is titrated at room temperature
with a 0.05 M solution of a salt of the metal to be
15 complexed (for example ferric chloride, cupric
chloride, calcium carbonate).

 The end point of the titration is visualised
by the onset of a sudden increase in the cloudiness of
the solution measured, for example, by means of a light
20 photometer.

 The complexing power is expressed as a molar
ratio sequestrant/metal ion: the lower this ratio, the

better the complexing power of the test compound.

Tests were carried out on various compounds:

- (A) pentasodium salt of N,N,N',N'-
tetra(carboxymethyl)-2,6-diaminohexanoic
5 acid (prepared in Example 1) (LYSTA);
- (B) pentasodium salt of N,N,N',N'-
tetra(carboxymethyl)-2,5-diaminopentanoic
acid (ORNTA);
- (C) tetrasodium salt of ethylenediaminetetraacetic
10 acid (EDTA) by way of comparison;
- (D) trisodium salt of 2-hydroxy-N,N-
bis(carboxymethyl)-3-aminopropionic acid
(or trisodium salt of isoserine-N,N-diacetic
acid:ISDA) by way of comparison (US 4, 827, 014).
- 15 The results obtained are collated in Table 1
below.

Examples	Sequestrants	Molar ratio sequestrant/ion		
		Ca ⁺⁺	Cu ⁺⁺	Fe ³⁺
20 3A	LYSTA	1/2	1/2	1/2
3B	ORNTA	1/1.5	1/1.5	1/1.3
3C	EDTA	1/1	1/1	1/0.4
25 3D	ISDA	1/0.6	1/1.6	1/4

TABLE 1

It is observed that the 2 compounds of the

invention have a substantially higher complexing power than EDTA which is commonly used in detergent compositions and that they also have a higher complexing power for calcium than ISDA, and of the same order of magnitude for copper as ISDA.

Example 4

Stabilisation of sodium perborate

A standard detergent composition of the following composition by weight is prepared:

10	-	sodium dodecylbenzenesulphonate:	7.0 %
	-	ethoxylated ketostearyl alcohol (11 moles of ethylene oxide):	8.0 %
	-	sodium tripolyphosphate:	25.0 %
	-	sodium metasilicate, 5 H ₂ O:	6.0 %
15	-	sodium perborate, 4 H ₂ O:	15.4 %
	-	sodium carbonate:	6.0 %
	-	anhydrous sodium sulphate:	32.6 %

Using this detergent composition, solutions at a concentration of 6.5 grams/litre are prepared in distilled water. Defined amounts (expressed in 10⁻⁶ g/g of solution or ppm) of Fe³⁺, Cu²⁺ and Mn²⁺ ions are added to these solutions as well as 0.9 % (by weight relative to the weight of the detergent composition in solution) of a sequestrant:

- 25 (A) pentasodium salt of N,N,N',N'-
tetra(carboxymethyl)-2,6-diaminohexanoic
acid (prepared in Example 1) (LYSTA): invention
- (B) pentasodium salt of N,N,N',N'-

tetra(carboxymethyl)-2,5-diaminopentanoic
acid (ORNTA): invention

(C) tetrasodium salt of ethylenediaminetetraacetic
acid (EDTA): prior art

5 (D) trisodium salt of 2-hydroxy-N,N-
bis(carboxymethyl)-3-aminopropionic acid
(ISDA): prior art.

These various solutions, as well as control
solutions without sequestrant, are maintained 2 hours
10 at 80°C.

After this treatment, the amount of
undecomposed sodium perborate is assayed in each of
these solutions.

The results obtained are collated in Table 2
15 below.

Examples	Fe^{3+} (in ppm)	Cu^{2+} (in ppm)	Mn^{2+} (in ppm)	Seques- trant	% of per- borate remaining
Control	0.6	0.25	0.25	None	0
4A	0.6	0.25	0.25	0.9 % LYSTA	42
4B	0.6	0.25	0.25	0.9 % ORNTA	51
4C	0.6	0.25	0.25	0.9 % EDTA	38
4D	0.6	0.25	0.25	0.9 % ISDA	21

TABLE 2

It is observed that the sequestrants of formula (I) of the invention are more effective than EDTA and, in particular ISDA of the prior art for stabilising sodium perborate.

$$\begin{array}{c} \text{H}_3\text{-OOC-H}_2\text{C} \\ \text{H}_3\text{-OOC-H}_2\text{C} \end{array} \text{N} \left(\text{CH}_2 \right)_n \text{CH} \begin{array}{c} \text{CH}_2\text{-COO-M}_3 \\ \text{COOH}_5 \\ \text{CH}_2\text{-COO-M}_4 \end{array} \quad (\text{I})$$

- n represents a number from 1 to 6,
- the symbols M_1 , M_2 , M_3 , M_4 and M_5 , identical or different, represent:
 - a hydrogen atom,
 - an alkali metal,
 - an ammonium group $-NH_4$ or an ammonium group substituted by 1 to 4 organic groups.

- n represents a number from 1 to 6,
- the symbols M_1 , M_2 , M_3 , M_4 and M_5 , identical or different, represent:
 - a hydrogen atom,

- a sodium or potassium atom,
- an NH_4 group,
- a monoalkylammonium, dialkylammonium, trialkylammonium or tetraalkylammonium group, the alkyl radical or radicals, linear or branched, having 1 to 4 carbon atoms.

5
10 3. Composition according to claim 1, characterised in that in the formula (I) of the sequestrants used:

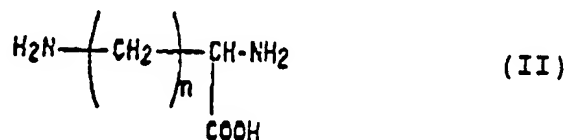
- n represents a number from 2 to 4,
- the symbols M_1 , M_2 , M_3 , M_4 and M_5 , identical or different, represent a hydrogen atom or a sodium atom.

15 4. Composition according to one of claims 1 to 3, characterised in that the sequestrant of formula (I) is chosen from the pentasodium or tetrasodium salts of N,N,N',N'-tetra(carboxymethyl)-2,6-diaminohexanoic acid,
20 the pentasodium or tetrasodium salts of N,N,N',N'-tetra(carboxymethyl)-2,5-diaminopentanoic acid
the pentasodium or tetrasodium salts of N,N,N',N'-tetra(carboxymethyl)-2,4-diaminobutyric acid.

25 5. Composition according to one of claims 1 to 4, characterised in that the sequestrant of formula (I) represents 0.01 % to 20 % and preferably 0.05 % to 10 % by weight relative to the total dry weight of the detergent composition.

6. Composition according to one of claims 1 to 5, characterised in that it contains 5 to 25 % by weight per weight of surface-active agents, 15 to 50 % by weight per weight of builders, with or without co-builders, 5 to 35 % by weight per weight of bleaching agents with or without activators of the said bleaching agents, and other constituents such as enzymes, antifoaming agents, corrosion inhibitors, brighteners, perfumes, colorants, formulation adjuvants, fillers and, optionally, water.

7. Process for preparing the sequestrants of formula (I) used in the composition according to one of claims 1 to 6, characterised in that they are obtained by reacting diaminocarboxylic acids of general formula (II):



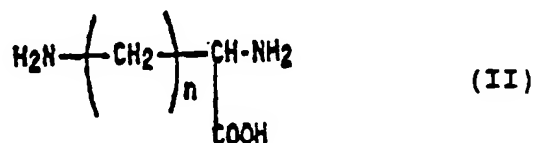
in which n represents a number from 1 to 6 and preferably from 2 to 4, with sodium chloroacetate.

8. Process according to claim 7, characterised in that the reaction is carried out in solution in water and at a temperature of 25°C to 100°C and preferably 40°C to 90°C.

9. Process according to one of claims 7 or 8, characterised in that the diaminocarboxylic acid of formula (II) is chosen from lysine (n = 4),

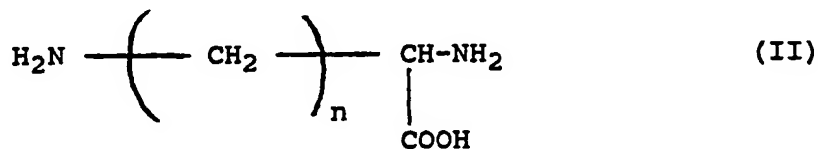
ornithine ($n = 3$), and 2,4-diaminobutyric acid ($n = 2$) and is preferably lysine.

10. Process for preparing the sequestrants of formula (I) used in the composition according to one of claims 1 to 6, characterised in that they are
 5 obtained by reacting diaminocarboxylic acids of general formula (II):



in which n represents a number from 1 to 6 and
 10 preferably from 2 to 4, with an alkali metal cyanide and formaldehyde, in the presence of water, at a temperature of 25°C to 100°C and preferably 40°C to 90°C.

11. Process for preparing a sequestrant of formula (I) used in the composition according to one of claims 1 to
 15 6, characterised in that it is obtained by reacting a diaminocarboxylic acid of general formula II



in which n represents a number from 1 to 6 and preferably from 2 to 4, with an alkali metal cyanide and formaldehyde,
 20 in the absence of water, at a temperature of 25°C to 100°C, and preferably 40°C to 90°C, and hydrolysing the resulting product.

- 23 -

Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number
 9123402.1

Relevant Technical fields

(i) UK Cl (Edition K) C2C CLU
 C5D DEX

(ii) Int Cl (Edition 5) C07C C11D

Search Examiner

D S LUCAS

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: CAS ONLINE

Date of Search

29 JANUARY 1992

Documents considered relevant following a search in respect of claims 1 TO 6

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	Chemical Abstracts 112(2): 106135u (UNIV. OF GRANADA)	1 to 6
X	Chemical Abstracts 109(26): 238263g (UNIV. OF GRANADA)	1 to 6
X	Chemical Abstracts 109(18): 157410a (UNIV. OF GRANADA)	1 to 6
X	Chemical Abstracts 106(4): 23955m (UNIV. OF GRANADA)	1 to 6
X	Chemical Abstracts 102(6): 51722u (UNIV. OF GRANADA)	1 to 6
X	Chemical Abstracts 97(2): 8578t (KALININ POLYTECHNIC)	1 to 6
X	Chemical Abstracts 87(4): 29839n (URAL POLYTECH. INST.)	1 to 6

Category	Identify document and relevant passages	Relevant to claim(s).

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

E) Examiner's report to Comptroller under
Section 17 (The Search Report)

Application number

9123402.1

Relevant Technical fields

(i) UK Cl (Edition K) C2C CLU

(ii) Int CL (Edition 5) C07C

Search Examiner

D S LUCAS

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: CAS ONLINE

Date of Search

20 MAY 1992

Documents considered relevant following a search in respect of claims

7 TO 11

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	Chemical Abstracts 105(23): 208376w (UNIVERSITY OF GRANADA)	7 to 9
X	Chemical Abstracts 102(5): 46238m (UNIVERSITY OF GRANADA)	7 to 9
X	Chemical Abstracts 100(13): 103831j (UNIVERSITY OF GRANADA)	7 to 9
X	Chemical Abstracts 93(8): 81513q (KALININ POL USSR)	7 to 9
X	Chemical Abstracts 86(18): 128301s (UNIVERSITY OF GRANADA)	7 to 9

Category	Identify document and relevant passages	Relevant to claim(s).

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).